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APPLICATION EFFICIENCY OF SODIUM-BASED INHIBITION SUSPENSIONS WHILE ROCK WASTE PROCESSING

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ABSTRACT

Is the determination of the processing efficiency of rock waste using sodium-based inhibiting suspensions to normalize the thermal state of the waste? The problems were solved through methods of mathematical statistics, a method of environmental assessment of options for a technological solution, and x-ray fluorescence analysis of the rock waste samples before their processing using inhibiting suspensions and after it. Indicator analysis of rock waste processing by means of the sodium-based inhibiting suspensions helps elaborate recommendations to use them at the initial stage of the rock waste formation for the provision of ecological stability of mining regions. Relying upon the research results, it has become possible to propose new methods to process rock waste with the help of sodium group solutions owing to which environmental impact on chemical processes within interstitial space of the rock waste is leveled. For the first time, such sodium-based soda solutions as sodium carbonate, sodium bicarbonate, and sodium hydroxide have been proposed to process rock waste mass. For the first time, it has been identified that the use of sodium-based inhibiting suspensions while rock waste processing helps minimize its interaction with the environment as well as the thermal oxidation reactions of the rock waste. The research has helped identify interaction between the rock waste mass samples taking into consideration the environmental impact. The proposed methods to perform processing using sodium-based suspensions have been applied for the combined rock waste treatment to avoid environmental risks for mining areas and forecast a level of environmental impact on the rock waste processed with the help of sodium solutions. The abovementioned will help reduce the probability for the development of sulfuric acid zones as the factor favouring rock waste self-ignition processes.

Keywords: rock waste processing, suspensions, sodium group, ecology, sodium carbonate, sodium bicarbonate, sodium hydroxide.

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INTRODUCTION

Rock waste, occupying significant area of useful land (taking into consideration protective sanitary area), is an integral part of coal mining enterprises [1, 2].

In the context of mining industry, processes of its waste combusting and oxidating result in the emission of harmful substances into the atmosphere. The harmful substances get into air, soil, and water objects from waste dump surfaces. When organic share of coal is heated in the oxidation chambers (cells), it experiences its thermal decomposition being similar to a pyrolysis process. As a result, such organic components as phenols, petroleum products, formaldehyde etc. are formed [3].

Production processes at mining enterprises generate following types of solid waste: overburden rocks, enclosing rocks, and preparation waste [4]. Generally, overburden and enclosing rocks are argillites, aleurites, clay, sand, sandstones, and other lithological and mineralogical types of rocks, varying in their composition, which restricts their wide national economic use [5]. Preparation waste as well as carbonaceous rocks, being of the most stable grade composition (namely, microelements and organic carbon) is of the greatest interest for industry. The abovementioned helps consider them as the specific type of so-called organic and mineral raw material, and apply as thermal generators for future gasification technology [6].

Conical shape coal mining waste is very prone to self-ignition; as a rule, it is formed during railway transportation of rocks. The waste height may be 20 up to 120 m with its following growth. The structure intensifies airflow towards the heap centre resulting in oxidation of inflammable material inside. It is recommended to place the waste dumps in such a way to direct prevailing wind to a tail part avoiding consequently their combustion [7].

Paper [8] describes self-ignition of waste dumps due to a chemical process involving high concentration of sulphur compounds. In combination with moisture, the compounds form a sulphur compound, which enters into oxidative reactions with rocks and carbonaceous inclusions resulting in thermal combustion. At a 3-5 m depth of the waste dumps, temperature may exceed 800^0-1000°C and a combustion process may last for decades.

According to its granulometric composition, rock waste is divided into coarse fraction (more than 13 mm); medium fraction (1-13 mm); and a fine one (0-1 mm). Most of all, fine waste is represented by flotation slurry. The waste is of nonuniform structure; i.e. it consists of fractions from different rock fragments varying in a diameter from 1.5 up to 400 mm. First, gravity deposits heavy 100-400 mm fraction; in such a way, a frame of the waste dump is shaped. Medium 50-95 mm fraction is the second layer; and a light 1.5-25 mm becomes its third layer. Hence, during the certain interval, rock contraction (compaction) takes place, favouring origination of thermal ignition zones [9].

Moisture penetration inside interfragmentary space exercises the key influence at the initial stage of a heap combustion resulting in heating as well as redox reactions where iron oxides and rocks, rich in pyrite, participate [10].

Rock waste demonstrates rapid pyrite oxidation with a sulphuric acid release [11]. In this context, there is a correlation relationship between the environment acidity and content of sulphates formed in the mass during pyrite oxidation. It is believed that the pyrite oxidation and sulphuric acid transition to underground water is the key reason of the abovementioned [12]. Like that, in the majority of cases, water in pyrite mines has an acid reaction since a free sulphuric acid being sulphide oxidation product is its component.

It has been identified that the self-ignition zones often demonstrate significant release of mineral salts (mainly, white, brown, and yellow in colour) which ash composition shows high content of iron and aluminum sesquioxides [13].

Rock waste contains such various combustible materials as pure coal, coal shales, argillites, coal and rock layers, and pyrite; moreover, coal content increases from small grades up to the large ones [14].

Combustion processes of the rocks vary depending upon following factors: a waste pile type; availability of storage technique; and geometry of the waste piles.

Rock waste also involves metal oxides catalyzing initiation of combusting zones (underlined): CaO, SiO_2, Al_2O_3, K_2O, Fe_2O_3, S, and TiO_2.

Only two types of waste piles are free from combustion: burned out (extinguished) waste dumps and the recultivated ones [11, 16, 17].

The best method to fight against self-ignition is its prevention while neutralizing. The measure helps preserve the waste mass for future processing.

For example, paper [10] proposes KOH-, K_2CO_3-, $Ca(OH)_2$-, and $CaCO_3$-based solutions to prepare rock waste; however, the idea did not get further development.
Among other things, recultivation, land reclamation, landscaping with special varieties of plants, repurposing, and generation of thermal energy (gasification) are the known procedures preventing self-ignition. Nevertheless, they have a number of disadvantages, which cannot help avoid it completely. While applying the inhibiting suspensions, we solve the topical scientific and research problem as for slowing down the redox chemical reactions in the rock waste (i.e. its self-ignition) providing in such a way stability of *waste dump-environment* system [18, 19, 20].

The processed waste rock mass is applicable for the future use in the strategic economy of Ukraine as a valuable source of rare earth metals since it contains 55 g/t of Germanium (which rate of return is from 3 g/t), 20 g/t of Scandium (which rate of return is from 10 g/t), 100 g/t of Gallium (which rate of return is from 10 g/t), and small quantities of Yttrium and Zircon. The total amount of rare earth elements may achieve 250 g/t [21, 22, 23, 24, 25].

LITERATURE REVIEW

Many scientists have studied the composition of chemical elements that provoke the emergence of coal mining waste combustion centres, and we should highlight one in particular: Zborshchyk M.P. and Osokin V.V. 1990-2000 years (study of processes provoking spontaneous combustion of waste heaps); Zubova L.H., Zubov O.R. and Zubov A.O. 2006-2022 years (research and justification of chemical processes in waste heaps that provoke combustion, development of methods for reclamation of waste heaps, development of technology for the extraction of rare earth metals from waste heaps); Mnukhin A.H. 1986-2019 years (studying the composition of chemical elements in waste heaps that provoke combustion processes, the impact of waste heaps on the environment, the use of waste heaps as raw materials of the future, development of technology for the extraction of rare earth metals from waste heaps); Vorobiov S.H. 2006-2010 years (developed a methodology for assessing the environmental hazard of waste heaps and determining a set of measures to reduce it, developed engineering measures to prevent the washing away of the top layer of waste heap rocks and its ingress into groundwater); Bosak P.V. 2018-2020 years (development of a method for minimising the harmful factors of waste water from coal mine waste heaps by arrangements a bioplato); Volotkovska Yu.O. 2013-2016 years (methodological recommendations on the environmental and economic assessment of the project for the extraction of minerals from coal spoil heaps in order to ensure the investment attractiveness of their exploitation as technogenic deposits); Saranchuk V.I. 1976-2005 years (theoretical description of the processes of spontaneous combustion and burning of waste heaps in coal mines, composition and distribution of waste heaps of different types, analysis of their fire hazard, causes of occurrence and ways to prevent deformation of burning waste heaps, recommendations on methods and means of preventing spontaneous combustion and extinguishing waste heaps); Pinder V.F. 2016-2020 years (a system for regulating the development of phytocoenoses involving Scots pine on waste heaps depending on the temperature of the waste rock substrate was developed, which ensures the environmental safety of the region and the implementation of environmental protection measures); Surnachov B.O. and Leonov P.O. 1958-1970 years (The causes and mechanisms of occurrence of hazardous phenomena in waste heaps, recommendations on technological safety measures in the operation of waste heaps, measures to eliminate deformations of the surface of waste heap slopes are considered). However, the monographs by M.P. Zborshchyk and V.V. Osokin "Prevention of spontaneous combustion of rocks, 1990"; "Prevention of environmentally harmful manifestations in rocks of coal mines, 1996"; "Combustion of rocks of coal mines and their extinguishing, 2000" pay considerable attention to the study of the influence of chemical elements on the

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occurrence of combustion of waste heaps and the mechanism of spontaneous combustion of waste heaps. The main causes of chemical leaching of pyrite and the main chemical components, which leads to the formation of thermal combustion concentrators (combustion centres), are highlighted.

METHODOLOGY

The research was intended to identify efficiency of sodium-based inhibitors.

The study has applied the three sodium-based solutions: sodium bicarbonate, sodium carbonate, and sodium hydroxide visualized in Figure-1 and Table-1; their chemical characteristics are also available.

Rock waste from a dump (Figure-2), put into operation in 1964 and put out of it in 1989, has been taken for the analysis. The waste pile belongs to a former T.H. Shevchenko mine (*Shakhtoupravlinnia Pokrovske* PJSC, town of Pokrovsk Donetsk Region). The burned rock waste (Figure-3, A) and the burning one (Figure-3, B) have been screened through 10 mm laboratory sieves.
The waste was sorted into the control and experimental groups.

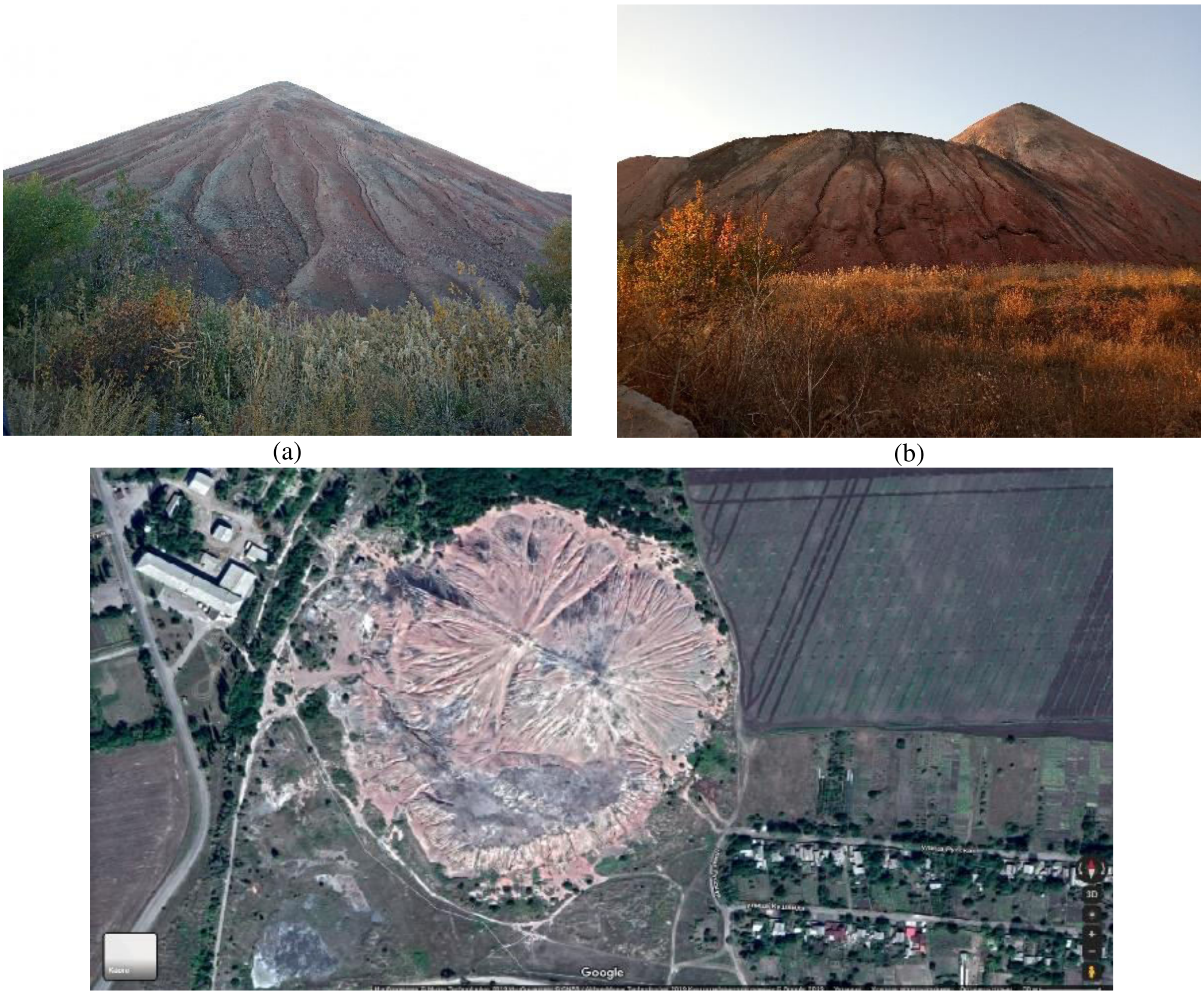
Since, the majority of granulometric composition of the rock waste consists of minerals which average fraction is more than 10 mm, three samples of the burned waste and three samples of the slightly burned one were selected for the study; the samples were studied through the x-ray fluorescent analysis.

A B C

Figure-1. Visualization of sodium powder applied to prepare the suspensions: A - sodium bicarbonate; B - sodium carbonate; and C - sodium hydroxide

Table-1. Chemical characteristics of sodium group.

Chemical characteristics	Sodium bicarbonate	Sodium carbonate	Sodium hydroxide
State/initial view	Solid/white powder	Solid/white powder	Solid/granular capsules
Chemical formula	Na_2HCO_3	Na_2CO_3	NaOH
Molar mass, g/mol	84.0066	105.99	39.997
Density, g/cm^3	2.159	2.53	2.13
-Melting temperature, C^0 -Decomposition temperature, C^0	-60 -200	-854 -1000	-323 -1403
Water solubility at $t=20^0$ C, g/100 ml	9.59	21.8	108. 7



(a) (b)

(c)

Figure-2. Waste pile of *Shakhtoupravlinnia Pokrovske*: A, B - general side view; and C - overhead view in the Explore Google Earth.

(a) (b)

Figure-3. General view of the rock waste: A -burnt mass; and B - slightly burnt mass.

The experimental methods can be expressed through a 'Black box' idea, i.e. when input parameters are known and output parameters are unknown, the rock waste mass is the target.

While applying mathematical theory of an active experiment, the model of rock waste mass processing by means of sodium-based suspensions may be represented as a structural pattern shown in Figure-4.

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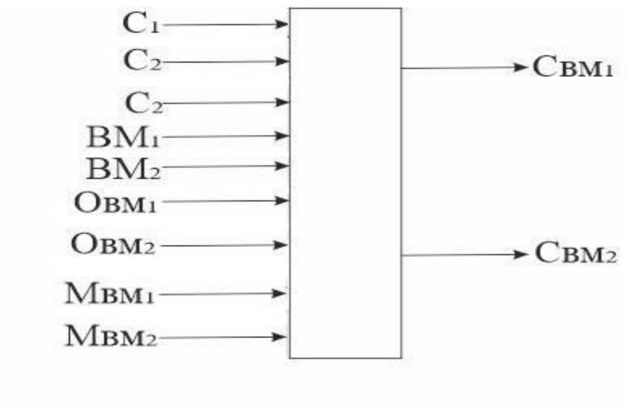
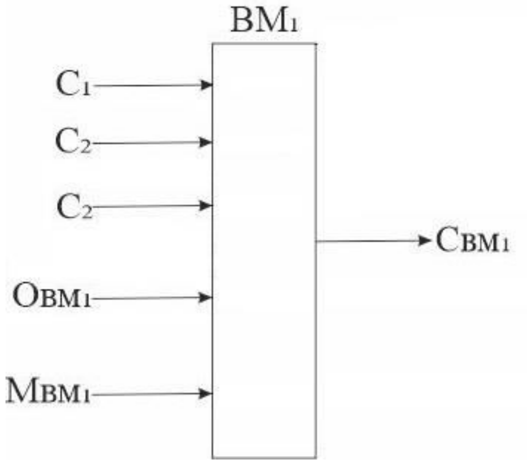


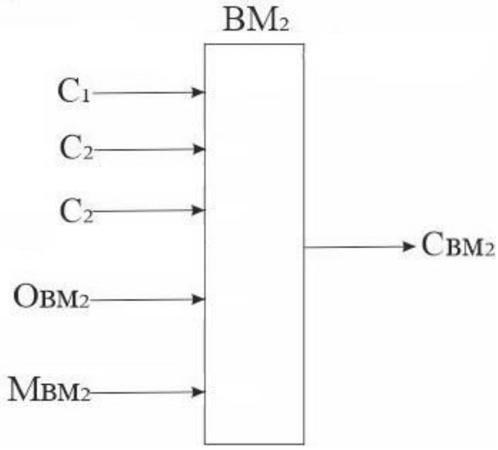
Figure-4. Structural pattern of input/output parameters to process rock waste by means of sodium-based suspensions.

C_1 - sodium bicarbonate suspension; C_2 - sodium carbonate suspension; C_3 - sodium hydroxide suspension; BM_1 - burnt rock waste; BM_2 - slightly burnt rock waste; O_{BM1} - slightly burnt rock waste processed using the suspension; O_{BM2} - burnt rock waste processed using the suspension; M_{BM1} - slightly burnt rock waste mass; M_{BM1} - burnt rock waste mass; C_{BM1} - slightly burnt rock waste mass processed using C_1, C_2, C_3 suspensions; and C_{BM2} - burnt rock waste mass processed using C_1, C_2, C_3 suspensions

The process of suspension use has been divided into two stages (Figure-5). Three samples of the slightly burnt rock waste (Figure-5, A), and three samples of the burnt rock waste (Figure-5, B) have been processed using NaOH, $NaHCO_3$, and Na_2HCO_3. Compare the output processing results with the rock waste mass before it was treated by means of the suspensions.



(a)



(b)

Figure-5. Structural pattern of input/output parameters to process rock waste by means of sodium-based suspensions: A - slightly burnt rock waste; and B - burnt rock waste.

The suspension was prepared as follows. 50 gr of hydrogen carbonate, carbonate and sodium hydroxide were added to a water filled 100-ml lab retort to make a 50% solution; water temperature was 20^0C.

The processing procedure was carried out in such a way. Spray device was used to sprinkle the rock waste by means the three suspension types: hydrogen carbonate, carbonate and sodium hydroxide with the total 50% concentration with further drying during a month.

The suspensions may be applied as inhibitors for the rock waste processing since they are the most available and cheap.

RESULTS

After the procedure (Figure-6), the rock waste samples demonstrated significant changes resulting from their treatment with the help of different sodium-based solutions. Sample 1, processed by means of sodium hydroxide, showed considerable SiO_2 oxidation, which content is 74 %, and Al_2O_3, which content is 17%, which is supported by its pinkness.

Sample 2, treated using sodium bicarbonate, did not demonstrate any significant changes.

Sample 3 experienced processing through the use of sodium carbonate. In this context, crystallization of the solution at the sample surface is observed. The abovementioned helps avoid further oxidation of the fragment porous structure within interfragmentary space of a dump as a result of environmental impact. As for samples 4, 5, and 6 where SiO_2 (silicon dioxide) prevails with its 65% content, and Al_2O_3 (aluminum oxide) content is 23 %, they demonstrate similar visual picture.

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Sample 1 (SBR) NaOH


Sample 2 (SBR) $NaHCO_3$


Sample 3 (SBR) Na_2HCO_3


Sample 4 (BR) Na_2HCO_3


Sample 5 (BR) NaOH


Sample 6 (BR) $NaHCO_3$

Figure-6. General view of the rock waste sample after they were processed by means of sodium solutions. SBR - slightly burnt rock; and BR - burnt rock.

X-ray fluorescence analysis of the rock waste samples (Figure-7), performed with the use of EXPERT 3L spectrometer (Figure-8), has helped identify proportional ratios (Table-2) which showed which chemical reaction of the rock waste mass took place while it's processing by means of NaOH-, $NaHCO_3$-, and Na_2CO_3-based suspensions (Figure-9).

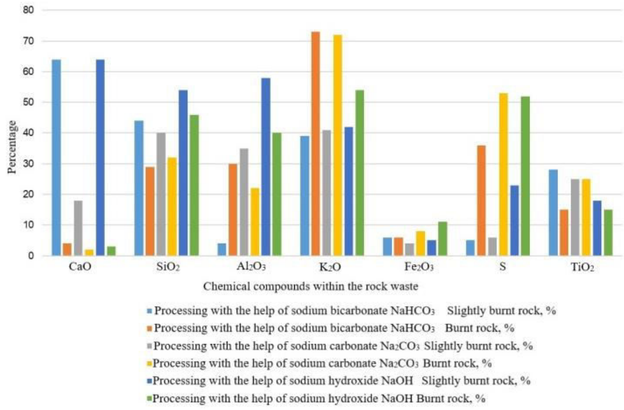

Figure-7. Diagram of difference indices during the rock waste treatment by means of sodium-based suspensions.

Figure-8. General view of EXPERT 3L spectrometer.

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Table-2. Proportional ratios of chemical elements within the rock waste after processing by means of the suspensions.

Suspension	Slightly burnt rock mass, %					Burnt rock mass, %				
	CaO	SiO_2	Al_2O_3	K_2O	TiO_2	SiO_2	K_2O	Al_2O_3	S	TiO_2
NaOH	64	54	58	42	-	46	54	40	52	-
$NaHCO_3$	64	44	-	39	28	29	73	30	36	-
Na_2CO_3	-	40	35	41	25	32	72	22	53	25

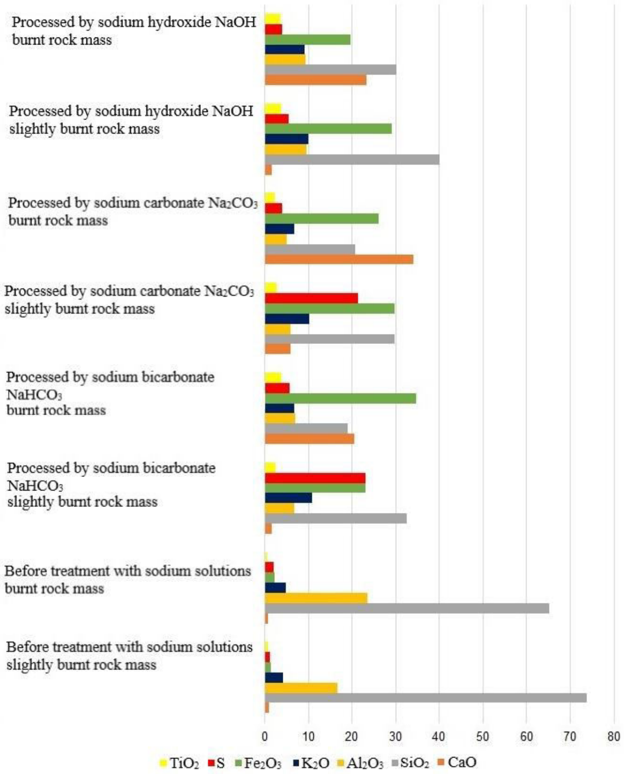

Figure-9. Diagram of X-ray fluorescence analysis indices of rock waste processing by means sodium-based suspensions before the procedure and after it.

CONCLUSIONS

Hence, while solving the problem of efficient rock waste processing, one can confirm that it is expedient to apply the sodium-based suspensions, namely sodium bicarbonate, sodium carbonate and sodium hydroxide. It has been identified that the suspensions influence heavily physicochemical processes within both slightly burnt and burnt rock waste mass decelerating development of thermal zones as a result of chemical oxidation of elements in the rock waste. Further, the processed rock waste may be applied for preparation to obtain rare earth metals.

The research, which applied sodium-based hydrocarbonate solutions, has demonstrated their advantage since they accelerate rock waste preservation processes and reduce its self-ignition risk. In such a way, the solutions, based upon sodium hydroxide, increase SiO_2, and Fe_2O_3 content; the solutions, based upon sodium carbonate increase SiO_2, Fe_2O_3, CaO, and S content; and the solutions, based upon sodium bicarbonate, increase Fe_2O_3, SiO_2, S, and CaO content.

High efficiency of the sodium-based solutions to avoid rock self-ignition can be explained by their influence on a solid phase as well as on a liquid one. Sodium hydroxide may interact with carbon dioxide, dissolved in water, and with free carbonic acid.

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